

A Novel Pattern of Dimerization for 1,4-Diphospha-1,3-butadienes

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ABSTRACT: A new example of [2+4] cycloaddition of the low-coordinated diphospha-analog of butadiene protected with a 2,4-di-*tert*-butyl-6-methylphenyl group has been described. X-ray structure investigations of monomer **4b** and dimer **5a** have been reported for the first time. © 2003 Wiley Periodicals, Inc. *Heteroatom Chem* 14:231–234, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10123

INTRODUCTION

The P=C π -bond in phosphalkenes is practically apolar [1–3]. As a matter of fact the polarity of this bond could be reversed by dialkylamino-substituents on the carbon side [4]. The regioselectivity by the addition of a polar reagent at the P=C π -bond can also be controlled by the type of substituents at the bond. Examples of proton addition to the different sides of P=C bonds, as well as hydride addition to the different sides upon variation of the substituent, are known [5,6]. This kind of tunability is of great interest in catalytic chemistry, where retaining the same metal with a variation of sterical or electronic factors around the ligand could result in the appearance of new technologies [7]. The phosphalkenes as a part of the chelating ligands have been in use for ethylene polymerization [8], hydroamination [9], and silylation [10]. The above-mentioned catalysts were based on the rigid 3,4-bis(phosphamethylene)-

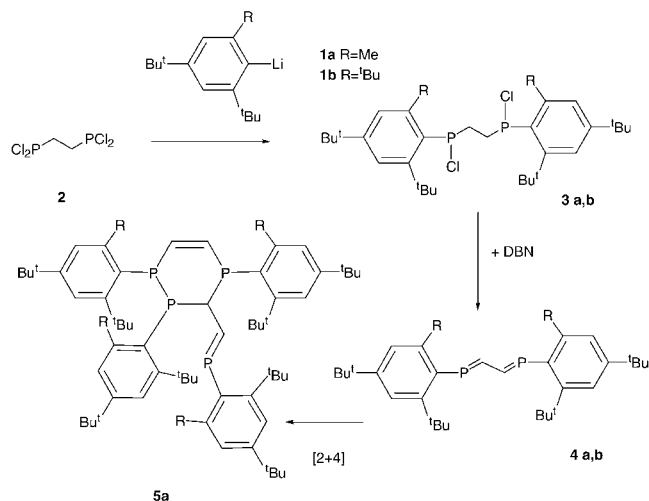
1-cyclobutene ligands [11]. Two examples of 1,4-diphospha-1,3-butadienes with more flexible backbones were described [12,13]. 2,3-Alkoxy-substituted 1,4-diphospha-1,3-butadienes undergo [2+2]-cycloaddition, leading to correspondingly substituted 3,4-diphosphacyclobutenes [13], unless sterically protected by a super-mesityl group to retard the self-dimerization by a [2+2]-motive [12]. The 2,4,6-tri-*tert*-butylphenyl group (super-mesityl) has been shown to be one of the best in supporting low coordination in phosphorus chemistry. However, it seems to be too sterically excessive in providing polymers with high molecular weight when compared with the α -diimines [7,8]. In this report, we describe a novel pattern of dimerization of moderately carbo-substituted 1,4-diphospha-1,3-butadienes.

RESULTS AND DISCUSSION

R. Appel's scheme [12] was used for generating 1,4-diphospha-1,3-butadienes. The 2,4-di-*tert*-butyl-6-methylphenyl group, which allows stabilization of diphosphenes [14], phosphalkenes [15], dithiophosphorane [16], and arsaalkenes [17], as well as the 1,4-diphospha-1,3-butadienes with a rigid cyclobutene backbone [18], was employed as a protection group. 2,4-Di-*tert*-butyl-6-methylphenyllithium (**1a**) was reacted with 1,2-bis(dichlorophosphino)ethane (**2**) in a molar ratio of 2:1, followed by the addition of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) to synthesize 1,4-diphospha-1,3-butadienes **4a,b** (Scheme 1). The intermediate 1,2-bis(2,4-di-*tert*-butyl-6-methylphenylchlorophosphino)ethane (**3a**) has two chemical shifts in the ^{31}P NMR at $\delta = 95.09$ and 94.71 ppm, because of the existence of two isomers. The 1,4-diphospha-1,3-butadiene **4a**

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SCHEME 1 Syntheses of 1,4-diphospha-1,3-butadienes **4a,b** and the dimerization of **4a**.

has been found to be unstable at room temperature and it underwent [2+4] cycloaddition to form the dimer **5a**. Elemental analysis, NMR spectroscopy, and X-ray analysis (Fig. 1) proved the structure of **5a**. For example, there is a downfield signal in the ^{13}C NMR spectrum at $\delta = 173.40$ ppm (doublet, $^1J_{\text{PC}} = 40.1$ Hz, phosphalkene sp^2 -carbon).

The Diels–Alder reactions of **4b** with only norbornadienes were published [19]. In our case, reducing the sterical bulk near the phosphorus atom by replacing one *ortho-tert*-butyl group with a methyl

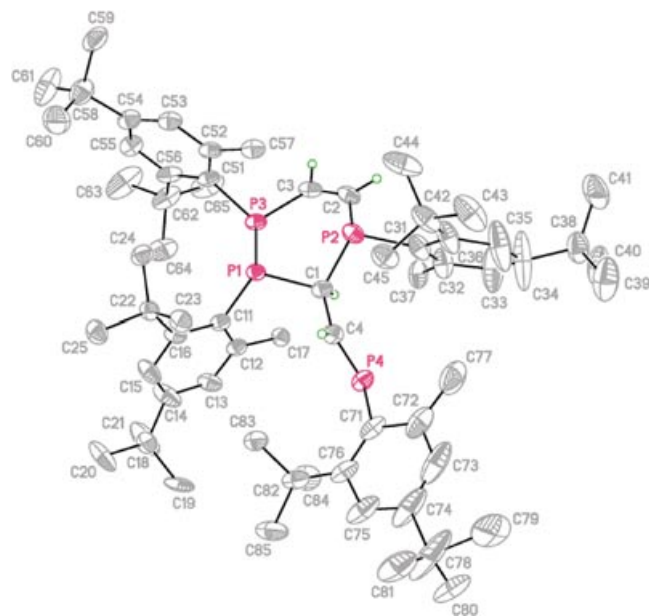


FIGURE 1 ORTEP drawing of the tetrahydro[1,2,4]triphosphinine **5a**. [Disordered positions and most hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn to the 50% probability level.]

group enhanced the dienophile properties of the 1,4-diphospha-1,3-butadiene **4a** as well as made the phosphalkene part of **4a** more accessible. The compound **4a** does not contain any substituents with a lone pair of electrons capable of altering the polarity of $\text{P}=\text{C}$ bond. This could also contribute to the [2+4] cyclization pattern of the dimerization of 1,4-diphospha-1,3-butadiene.

Although 1,4-diphospha-1,3-butadiene **4b** has been prepared [12], its X-ray structure has not been reported yet. The bond lengths of the 1,4-diphospha-1,3-butadiene moiety of **4b** contain the essential information about conjugation and the participation of the phosphorus atoms in the process. The small crystals of **4b**, which were suitable for X-ray analysis using synchrotron radiation, were grown from a toluene solution. The structure is shown in Fig. 2.

For example, the bond length between C(1) and C(1a) is 1.419(6) Å, which is shorter than 1.49(2) Å as reported for the 1,4-diphospha-1,3-butadiene with phenylthio-substituents in the 2,3-positions [20]. This could indicate a stronger conjugation in 2,3-unsubstituted 1,4-diphospha-1,3-butadienes.

In conclusion, we successfully demonstrated a novel pattern of dimerization for 1,4-diphospha-1,3-butadienes without rigid backbones. The molecular structures of the monomer **4b** and the dimer **5a** were determined by X-ray analysis. Their catalytic properties are now under investigation and will be reported in due time.

CCDC contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). The deposition numbers are CCDC 192384 & 192385 for **4b** and **5a**, respectively.

EXPERIMENTAL

1,4-Bis(2,4,6-tri-*tert*-butylphenyl)-1,4-diphospha-1,3-butadiene (**4b**)

The compound **4b** was prepared by the dehydrohalogenation procedure with DBN (1,5-diazabicyclo[4.3.0]non-5-ene) as described [12]. 1,2-Bis(2,4,6-tri-*tert*-butylphenylchlorophosphano)ethane (4.8 g, 0.0074 mol) was used for the preparation of **4b**. The yield of **4b** as a yellow solid was 1.49 g (35%), with mp 261.4°C. ^1H , ^{13}C , and ^{31}P NMR data were practically identical with the reported values; for example, ^{31}P (500 MHz, CDCl_3) $\delta = 270.91$ against 269.5 ppm for the major isomer.

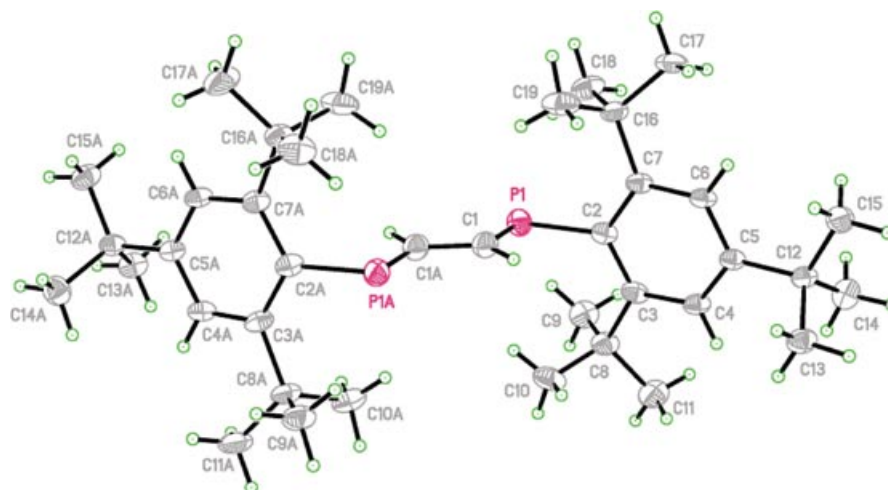


FIGURE 2 ORTEP drawing of the 1,4-diphospha-1,3-butadiene **4b**. [Thermal ellipsoids are drawn to the 50% probability level.]

1,2,4-Tris(2,4-di-tert-butyl-6-methyl-phenyl)-3-(2,4-di-tert-butyl-6-methyl-phenylphosphanylidene)methyl-1,2,3,4-tetrahydro-[1,2,4]triphosphinine (5a)

The compound **5a** was prepared by the same dehydrohalogenation procedure with DBN (1,5-diazabicyclo[4.3.0]non-5-ene) as described [12]. 2-Bromo-1,5-di-tert-butyl-3-methyl-benzene (5.37 g, 0.019 mol) and 1,2-bis(dichlorophosphino)methane (2.0 g, 0.0086 mol) were used for the preparation of **5a**. The yield of **5a** as slightly yellow solid was 1.15 g (27%), with mp 124.8°C. ^1H NMR (CD_2Cl_2) δ = 1.06 (s, broad, 36H, *t*-Bu), 1.62 (s, broad, 36H, *t*-Bu), 2.20 (s, 3H, Me), 2.25 (s, 3H, Me), 2.30 (s, 3H, Me), 2.45 (s, 3H, Me), 6.1–7.95 (m, 11H, aromatic and =C–H protons). ^{31}P NMR (CDCl_3) δ = –34.74 (dd, $^1J(\text{PP})$ = 197.5 Hz, $^3J(\text{PP})$ = 37.3 Hz; (P-1)), δ = –16.97 (d,d,d, $^1J(\text{PP})$ = 197.5 Hz, $^2J(\text{PP})$ = 41.4 Hz, $^3J(\text{PP})$ = 34.6 Hz, (P-2)), δ = –9.04 (d,d, $^2J(\text{PP})$ = 41.4 Hz, $^3J(\text{PP})$ = 37.3 Hz, (P-3)), δ = 256.16 (d, $^3J(\text{PP})$ = 34.6 Hz, (P=C)). Anal. Calcd (%) for $\text{C}_{64}\text{H}_{96}\text{P}_4$: C, 77.70; H, 9.78; P, 12.52. Found: C, 77.51; H, 9.51; P, 12.38.

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REFERENCES

- [1] Dillon, K. D.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998; pp. 1–14.
- [2] Quin, L. D. *A Guide to Organophosphorus Chemistry*; Wiley: New York, 2000; pp. 307–345.
- [3] Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O. J. (Eds.); Georg Thieme Verlag: Stuttgart, 1990; pp. 157–219.
- [4] Patsanovskii, I. I.; Ishmaeva, E. A. *Zh Obshch Khim* 1993, 63, 2552–2568.
- [5] Meriem, A.; Majoral, J.-P.; Revel, M.; Navech, J. *Tetrahedron Lett* 1983, 24, 1975–1978.
- [6] Ermolaeva, L. V.; Ionkin, A. S. *THEOCHEM* 1992, 95, 25–33.
- [7] Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem Rev* 2000, 100, 169–1203.
- [8] Ikeda, S.; Ohhate, F.; Miyoshi, M.; Tanaka, R.; Minami, T.; Ozawa, F.; Yoshifuji, M. *Angew Chem, Int Ed* 2000, 39, 4512–4513.
- [9] Minami, T.; Okamoto, H.; Ikeda, S.; Tanaka, R.; Ozawa, F.; Yoshifuji, M. *Angew Chem, Int Ed* 2001, 40, 4501–4503.
- [10] Ozawa, F.; Yamamoto, S.; Kawagishi, S.; Hiraoka, M.; Ikeda, S.; Minami, T.; Ito, S.; Yoshifuji, M. *Chem Lett* 2001, 10, 972–973.
- [11] Appel, R.; Winkhaus, V.; Knoch, F. *Chem Ber* 1987, 120, 243.
- [12] Appel, R.; Hünerbein, J.; Siabalis, N. *Angew Chem, Int Ed* 1987, 26, 779–780.

- [13] Appel, R.; Barth, V.; Knoch, F. *Chem Ber* 1983, 116, 938–950.
- [14] Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Matsushita, T.; Nishimoto, K. *J Am Chem Soc* 1983, 105, 2495–2497.
- [15] Baudler, M.; Joachim, S. *Chem Ber* 1988, 121, 281–285.
- [16] Ionkin, A. S.; Nekhoroshkov, V. M.; Efremov, Y. Y. *Izv Akad Nauk SSSR, Ser Khim* 1991, 7, 1654–1656.
- [17] Ionkin, A. S.; Nikolaeva, N. V.; Musin, R. Z.; Efremov, Y. Y.; Arbuzov, B. A. *Phosphorus, Sulfur Silicon Relat Elem* 1992, 66, 257–260.
- [18] Yoshifuji, M.; Ichikawa, Y.; Toyota, K.; Kasashima, E.; Okamoto, Y. *Chem Lett* 1997, 1, 87–88.
- [19] Siabalis, N. *Dissertation, Bonn*, 1989.
- [20] Ito, S.; Yoshifuji, M. *Chem Lett* 1998, 5, 651–652.